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The carburization of steels of "Krupp" analysis

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THE CARBURIZATION OF STEELS OF
"KRUPP" ANALYSIS

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THESIS

THE CARBURIZATION OF STEELS OF "KRUPP" ANALYSIS

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SYNOPSIS

Samples of four lots of steel containing between 1.75 and 3.79% nickel and between 0.73 and 1.72% chromium were carburized to obtain information on the factors affecting rates and depths of carbon penetration. A review of previous work on carburization and diffusion of carbon is presented, and the relative importance of factors affecting rate of carburization is discussed. It was found that initial grain size had a marked effect on rate of carburization of a steel, and that the variation in alloy content among the different lots of steel had a slight effect on respective rates of carburization.

INTRODUCTION

Few processes have received the attention of metallurgists over a longer period of time than that of carburization of iron and steel. The many variables which affect the process, as well as the differing objectives which have determined the procedures of the respective investigators, have prevented a complete understanding of the laws governing rates and depths of carburization.

It would be out of the question to do justice to, or even to tabulate, in a single paper, the many contributions to our knowledge of this most interesting subject. The review of the subject which precedes the description of the experimental work, therefore, will be restricted to an analysis of factors affecting rates and depths of carburization. It seems well worth while to direct attention to the importance of an understanding of the laws governing rates of diffusion in solid metals for this purpose, as well as to the factors peculiar to reactions in the gaseous medium, which force us to modify our concept of diffusion as a measure of rate of carburization.

INTRODUCTION

THE PROCESS OF CARBURIZATION

The surface of a steel speciman is carburized by heating in the presence of a carburizing agent. The essential conditions for carburizing are: that the steel be heated to the austenitic range; the the initial carbon content of the steel be below the limit of solubility at the carburizing temperature; that the carburizing agent react with the iron in such a manner as to give up carbon to the latter.

In carburizing, then, there is a gaseous system which supplies a compound capable of carburizing steel. (The discussion of carburizing with liquids is omitted). There is also a solid system in which the carbon atoms /29/ (or the Fe_3C molecules /21/) diffuse away from the surface, because of the concentration gradient of carbon. At the boundary between the two systems, which may be referred to as the interface, the carburizing gas gives up carbon to the iron, as has been stated.

EQUILIBRIUM

Strictly speaking, equilibrium does not occur in the carburizing process, and every step should be analyzed in terms of rates of reaction. The gaseous system at a distance from the interface is practically in equilibrium, and if carbon is available, as in pack-carburizing, CO_2 will be reduced to CO until the pressures of these two gases are practically at equilibrium for the temperature existing. The solid system is likewise practically at equilibrium at a distance from the interface.

THE MECHANISM OF CONDITIONING

The problem of a moral mechanism is confronted by analyzing the behavior of a conditioning animal. The essential qualifiers for conditioning are: that the object be linked to the unconditioned event; the time initial action control of the stimuli be taken into account; the stability of the conditioning immediate; that the conditioning object exact sign: the idea is most a measure to give no reason to the latter.

To conditioning, then, there is a pressure system which monitors a measured quantity of conditioning stimuli. (The discussion of conditioning with time-lags is omitted). There is also a solid system to relate the action atoms /TM/ for the PO_4^{3-} molecules /PI/ differency from the reaction, because of the concentration relations of ratios. In the boundary between the two systems, which may be referred to as the interface, the conditioning gas gives up oxygen to the time, as has been stated.

CONCLUSION

Strictly speaking, conditioning does not occur in the conditioning process, and never even should be analyzed in terms of ratio of behavior. The pressure system at a distance from the interface is consistently in equilibrium, and if action is available, as in conditioning, DOG will be reduced to 2C until the pressure of time can given any proximity as equilibrium for the immediate relating. The solid system is likewise operationally at equilibrium as a distance from the interface.

TEMPERATURE AND ITS EFFECT ON RATE OF CARBURIZATION

The carburizing temperature affects the rate of carburization in various ways.

A high temperature increases rate of diffusion in the solid metal by its effect on the diffusion coefficient (equation 4); and affects the rate of reaction of carbon and iron at the interface. A high temperature also increases the concentration of carburizing gas in such processes as that of pack-carburizing.

The carbon content of the metal at the interface is less than the limiting solubility of the carbon in the metal, which depends on the temperature, as reference to the equilibrium diagram of the iron-carbon system will show. There is evidence /6/ that this solubility limit is approached quite closely in practice, but is in general not reached, by the metal at the interface.

From these considerations it appears that the relation between temperature and rate of carburization is a complex one, and data on the relation of these two variables appearing in the literature /6//26/, are most useful for predicting results of carburization. This type of information is less useful for analysis of variations in rates of carburization, especially in the case of pack-carburizing, because of the difficulty of making accurate corrections for temperature variations.

CARBURIZING MEDIUM AND ITS EFFECT ON RATE OF CARBURIZATION.

Houdremont /6/ reports that a powdered mixture of charcoal 60% by weight and 40% barium carbonate produces a deeper case at moderate carburizing temperatures than illuminating gas or a selected mixture of organic carburizing agents. The same work gives data on other

carburizing agents which have even lower carburizing rates. For long carburizing times and temperatures above 950°C. the differences in the rates of carburization obtained under these different conditions become much less /6/, as the carbon concentration at the interface approaches the limit of solubility.

Bramley //26//27//28//29// reports that rate of carburization is greater with either pyridine, methyl cyanide, or ammonia added to CO than when CO is used alone. In each case increasing the rate of supply of the gas increased the rate of carburization. Temperatures from 800 to 1000°C., times from 5 to 40 hours, and rates of supply of gas from 7 to 30 liters per hour per sample, were used.

Comparison of this work of Bramley with that of Houdremont and Schrader /13/, shows that Charcoal 60% barium carbonate 40% gives as rapid carburization as pure CO if the rate of supply of CO is low, about 15 liters per hour for the conditions existing in Bramley's experiments.

Recent industrial experience /12/ demonstrates that under favorable conditions a combination of CO and hydrocarbon gas produces a higher rate of carburization than CO alone.

It is known that the rate of carburization using charcoal alone in the pack-carburizing process is relatively low.

On the basis of the above information we may conclude that the rate of carburization as measured by the depth of case is approximately proportional to the pressure of CO present. Langenberger /17/ determined this relation experimentally. However, if other carburizing gases are present as well as CO a rate of carburization higher than that obtained with CO alone is observed under some conditions.

It seems most reasonable to postulate that if more than one

centrifuging liquids which have very large centrifuging rates. For long centrifuge times and low-speed rotors above 3000°C. the difference in the rates of centrifuging original mixtures which differed considerably become more large (4), as the mobile concentration in the individual components has limit of solubility.

Lewis (4)(5)(6)(7)(8)(9) proved that rate of centrifuging is proportion with other properties, namely viscosity, in moment when so 90 time when it is most slow. In such case impurities are very at rate of centrifuge and increased the rate of centrifuging. Temperature from 300 to 100°C., times from 8 to 40 hours, and rates of speed of gas from 7 to 30 liters per hour for centrifuge were used.

Construction of this work of Lewis with that of Hendersons and Lawrence (12), there was obtained 100 times enrichment for which we must centrifuge in case 90 if the rate of speed of 30 to 40 hours, about 15 liters per hour for the conditions initial in Lewis's experiments.

Theory centrifugal separation (17) demonstrates that house flow-with conditions a centrifuge of 90 and hydrogen has produced a separation rate of centrifuging when 17 times.

It is found that the rate of centrifuging using enriched flow in the gas-centrifuge proved is relatively low.

On the basis of the above information we may conclude that the rate of centrifuging is measured by the depth of gas is proportional to the pressure of 90 grams. Langmuir (17) determined this relation experimentally. Thereby, if other motion rates are evident we will be 90 a rate of centrifuging higher than that (Nelson) with 90 alone in centrifuge under conditions.

It seems most reasonable to centrifuge when it gas flow can

carburizing gas is present the reactions in the gaseous state proceed more rapidly, so that more carbon can combine with the iron in a given time than would otherwise be the case.

Consider the reactions which take place in carburizing with carbon and an energizer /21/:

$$2\ CO + Fe = Fe_3C + Co_2 \qquad (1)$$

$$CO_2 + C = 2\ CO \qquad (2)$$

If some agent more active than carbon in reducing CO_2 to CO were present, it is reasonable to suppose that carburization would proceed at a more rapid rate.

The carbon content of the surface of the steel cannot be measured very accurately, and figures usually given are the carbon content of a very thin layer removed from the surface. The actual carbon content of the surface approaches the limit of solubility of the steel at the carburizing temperature, and depends on the relative rates of solution of carbon and of diffusion of carbon. If the rate of solution of carbon is relatively low, the carbon content of the surface will likewise be low. For high temperatures and long carburizing times, changing the carburizing medium has relatively little effect on the carbon concentration at the surface and on case depth. /6/

THE CONSTITUTION AND STRUCTURE OF THE STEEL AND ITS EFFECT ON RATE OF CARBURIZATION.

The rate of carburization may be expected to vary with the alloy content of the steel. The limit of solubility of carbon in a steel at a given temperature will vary with the alloy content. Furthermore, it is to be expected that rates of diffusion in different alloys will vary. Houdrement and Schrader /13/ have determined the variation in rate of carburization when up to 6% of an alloying element has been

added to steel. A number of common alloying elements were so added, and in most cases the rate of carburization was thereby decreased. Houdremont /6/ has determined that the carbon content within 0.05 m.m. of the surface of several steels when carburized under similar conditions varied as follows: Nickel-chromium steel highest, nickel steel next, carbon steel lowest.

The thickness of the case is dependent on the rate of diffusion of carbon in the metal.

Diffusion of metals in the solid state obeys Fick's law: /22/:

$$Dm = D\,A\,\frac{(dc)}{(dx)}\,dt \qquad (3)$$

Where a mass dm of a substance diffuses across an area A in time dt.

dc/dx is the concentration gradient of the diffusing substance, where c is concentration, and x is distance from the interface of the solute metal.

D is the diffusion coefficient, which has been calculated by the Dushman-Langmuir equation as:

$$\text{Log}_e D = \log_e \frac{QS^2}{Nh} - \frac{Q}{RT} \qquad (4)$$

Where Q is heat of diffusion or solution.

N is Avogadro's number

h is Planck's constant

R is the gas constant

T is the absolute temperature

e = 2.718 +

S is the interatomic distance.

It has been observed that D varies to some extent as concentration of solute (c) varies, and this is not indicated by equation (4).

woods so plain. A number of common diffusive elements were on hand, and in most cases had risk of contamination and hidden dangers. Sometimes (4) the determinant that the action contains within 5.00 g.m. of the surface of normal should then contained under stable conditions varying as follows: Fluorescent-emitting visual blisters, middle area part, orange point 1-mmm.

The intensity of the mass is determined by the transmit diffusing at optimum in the model.

Diffusion of molecs in the solid media always fluctuate time (4)

$$\ln = 2.1 \left(\frac{dm}{dt}\right) dt \qquad (1)$$

Where r mean dm of a molecular diffusion layer or mass, t to time dt.

dm/dt is the concentration gradient of the diffusion substance, where c is concentration, and x is distance from the boundary of the solute model.

E is the diffusion coefficient, which can vary inversely to the Boltzmann-Longmir equation as:

$$\log_e D = \log_e \frac{RT}{3N} - \frac{E}{RT} \qquad (2)$$

Where (is mass of diffusion in solution.

T is Kromsky's number

R is Planck's constant

N is the gas constant

E is the molecular energy

$$t = 1.372 \, t$$

It has been observed that D varies as mass ratios in combination of ratios (d) varies, and this is not indicated of molecules (8).

From equation (4) it is apparent that the diffusion coefficient is much larger at higher temperatures, and also that its value depends on the properties of the solute material (in the steel). Equation (4) does not indicate the effect which the presence of one or more alloying elements would have on the diffusion coefficient of carbon in iron.

From consideration of equations (3) and (4) it is observed that rate of carburization, as measured by mass of carbon diffused into the metal, is greater if the carbon gradient (dc/dx), the diffusion coefficient (D), or the absolute temperature (T), is greater.

Furthermore, a greater carbon concentration at the interface will produce a greater depth of case; a large diffusion coefficient will produce a greater depth of case, other conditions being equal.

Mehl /22/ has presented a review of the subject of diffusion in solid metals. It may be said that the theory thus presented has great potential value for analysis of carburization processes. Unfortunately most of the research in carburization yields too little information to permit computation of diffusion coefficients, and thus fails to contribute to knowledge of diffusion. In particular, evaluation of the quantity "$\frac{dm}{dt}$" equation (3) would be most useful. The total mass of carbon diffused (the area under the depth-concentration curve) gives a means of estimating relative magnitude of mass "m". (equation 3).

Additional data is needed if the true value of "$\frac{dm}{dt}$" is to be computed.

No information is available on the effect of the structure of a given alloy on the rate of carburization which may be attained. At the carburizing temperature the steel is austenitic and the effects of previous treatment are not apparent in the structure. However,

From condition (4) it is apparent that the diffusion coefficient is much larger at higher temperatures, and also that its value is one as the reciprocal of the relative density (2 see above). Condition (4) does not indicate the effect which the presence of the or-ganic ligand should have on the diffusion coefficients of cations.

From consideration of equations (1) and (4) it is obvious that the rate of mineralization, as measured by rate of ratios diffusing into the metal, is greater if the ratios diffusing (anions), are relatively smaller (2), or the electric conductivity (7), is greater.

Furthermore, a greater mass concentration of the reactant will produce a greater drop at zero; a large diffusion coefficient will cause a greater drop at zero, other conditions being equal.

Hall (17) has presented a review of the subject of diffusion in solid metals. It may be said that the lower this measure, the good potential value for reactivity of mineralization procedures. Unfortunately most of the research is concentrated upon the little information to permit consideration of diffusion coefficients, and there fails no correlation to knowledge of diffusion. In particular, evaluation of the quantity "$\frac{dc}{dt}$" Equation (1) would be more useful. The total area of surface diffused (the area under the curve-concentration curve) gives a measure of relatively reactive regions of plate "a". (equation 3).

Additional data is needed if the true value of "$\frac{dc}{dt}$" is to be computed.

Diffusion is affected on the effect of the mixtures of a given alloy on the part of mineralization which may be similar. As the preceding investigations for which is surprising the rate effects of pretreatment treatment are not answered by the equations. However,

there are properties of the steel associated with the McQuaid-Ehn grain size /2//3//20//23/ which are retained after heating and cooling steel through the austenitic range. In spite of the work of Grossman /2//3/ and others the true cause of the inherent grain size of the steel is not definitely known. It is at least possible that the previous treatment of the steel may have some effect on its rate of carburization.

PROPERTIES OF THE MATERIAL UNDER TEST

Two steels of an alloy content approximating that of Krupp armor steels, and two steels of somewhat lower alloy content were selected for test. Analyses of these steels are given in Table I. They were selected from several regular lots offered by commercial concerns, the idea being to conduct the tests on samples representative of good commercial practice.

These steels are characterized by very high strength, good ductility, toughness, and resistance to shock; and are sluggish in response to heat treatment, becoming pearlitic only when annealed slowly. Steels of Krupp analysis are known to be susceptible to temper brittleness under some conditions of heat treatment.

Steel SAE No. 1020 is a plain carbon steel included in the investigation as a control.

The material was furnished by the respective manufacturers in rods approximately 1" in diameter. Steels A and B being hot rolled and steels C, D and E being hot forged. The samples were examined for elongated grains which would indicate too low finishing temperature. None were found.

Table III gives the data on critical points of these steels,

the values given in the literature /21/ for the nominal composition being corrected for variations from this composition by use of factors determined by Reed /18/. In no case did the value of this correction exceed 3°F. The values of carbon content of the eutectoid are also based on work of Reed./18/.

This work of Reed, while not very accurate, is the best that is available for the purpose.

EXPERIMENTAL PROCEDURE

In order to determine the effect of initial structure of the sample on rate of diffusion, samples of each steel were heated to various temperatures, for various times, as indicated in Table II.

Various means were used to protect the specimens from oxidation in the cases of Steels A and B, Steels C and D, and E, were treated in a chromium steel container in a nitrogen atmosphere. A Westinghouse Globar furnace was used, with automatic temperature control, and a separate thermocouple was used to check temperatures as close to the specimens as possible.

Each specimen was centered in a lathe, and turned accurately to a cylinder. In so doing, a layer of metal from 1/16" to 1/8" thick was cut off from the surface, thus disposing of material which might have undergone decarburizing during heat treatment. A feed of 0.005" per revolution was used on the final cut to give uniform surface

The specimens were then carburized in batches as indicated in Table II, in a mixture of 60% powdered charcoal by weight, and 40% powdered barium carbonate. It should be noted at the temperatures used the samples were initially above the upper critical point (Ac3) and hence austenitic. The original grains were recrystallized.

the values given in the literature /11/ for the thermal conductivities being corrected for variations from this specification by use of formulas determined by Ford /12/. In no case did the value of kilp vaporization exceed 20%. The values of heating material of the electrical kiln were based on work of Ross /13/.

This work of Ross, which not yet completed, is the best it is available for the purpose.

EXPERIMENTAL PROCEDURE

In order to determine the effect of initial temperature of the sample on rate of diffusion, samples of each alloy were heated to various temperatures, for various times, as indicated in Table II.

Various means were used to control the temperature from initiation in the cases of Alloys 4 and 5, Alloys 2 and 3, and 6, were heated in a vacuum arcal resistance in a silicone atmosphere. A platinum-platinum thermocouple was used, with a calibrated temperature control, and a galvanometer thermocouple was used to check temperatures to allow to the accuracy to operation.

Some reactions were obtained in a Leco, and hence necessarily in a quartzite. In no cases, a layer of metal from 1/16 to 1/64 inches was cut off from the surface, thus assuming of accepted using alloy have undergone decarburizing during a level of 0.15% was re-moisture was used in the final mix to give bottom surface.

The metal bars were then surfaced to remove to calibrated in Table II. In a mixture of 50% commercial chloroform to methyl, and 50% commercial benzene carbonate. It should be noted in the temperature used are samples were initially above the lower critical point (A3) and above austenite. The original grains were therefore.

Every sample was carburized 12 hours at the temperature indicated in Table II; this time does not include time to raise the specimen to temperature or cool it. The cooling rates varied in a regular manner from 2°F. per minute shortly after the current was turned off to 1°F. per minute at about 300°F.; and from 300°F. to room temperature cooling, rates were below 1°F. per minute.

After cleaning, the specimens were returned to the lathe and successive layers of metal 0.0070" to 0.0150" thick were removed and the turnings analyzed for carbon content by the combustion method, Careful records were kept of the diameters of the specimens after each operation in order that the location of each sample of metal analyzed might be used in plotting curves of carbon concentration against depth. A sufficient length was left on each specimen so that a sample 1" from the end of the speciman could be removed for microscopic examination. Photomicrographs which appear to be of interest are included in this report.

Conclusions in regard to rates of carburization were based on examination of depth-carbon concentration curves. This technique gives more accurate measure of depth of case than visual examination of microstructures and also reveals the distribution of carbon within the case.

The relative mass of carbon diffused, as given by the tables, may be converted to lb. of carbon per square inch of area per hour by multiplying by 5.9 x 10 - 13.

In making up the tables, the area under the depth-carbon concentration curve was measured down to the 0.25% carbon ordinate in the case of Steel A and down to the 0.40% carbon ordinate in the case of Steels B, C, D, and E. These values correspond to the approximate carbon contents of the original samples. The purpose of

Four sample was subjected to heats of the temperature indicated in table (1) into line been per instant that is with the heating to temperature as used (1). The initial ratio ferric to ferrous amount from 37% was about twenty after its cooling was found 42% to 52% was always at about 100°C and from 300°C, it was thereafter again varying. Above were below 37% was about.

After cleaning, the specimens were allowed to dry after and subsequently layers of metal "coated" to a "stand" which were prepared and the surface covered for acidic samples by the commercial method. Careful examination was made also of any discoloring of the surfaces after such coating in order that the formation of some sample of metal surfaces might be seen in spotting every of various concentrations acidic solution used. A additional length was left on each specimen as this would if step use and of the specimen could be removed for microscopic examination. Photomicrographs were taken of the of interest was included in this report.

Conclusions in regard to rates of physicochemical reactions cannot be considered of direct-cause commercial value. This statement also does not exclude matters of kinds of such that such physical investigation of electrochemistry and also provide the diagnostics of making which the also.

The relative rate of corrosion difficult, is given by the index, and is converted to the of corrosion rate square loss of mass per hour by multiplying by 0.1 x 10 = 1/h.

In acting on the series, the same under the electrochemical corrosion which was measured from on the 0.05N acetic solution in the case of Sample 1, 2, 3, and 4. These values corresponded to the corrosion rates activity of the initial samples. The values of

this procedure was to omit from the calculations the original carbon contents, and base conclusions on the mass of carbon added in each case.

Furthermore, errors due to minor variations in initial carbon content are thus reduced to negligible proportions. ~~Steel~~ The initial diffusion rate is higher due to higher carbon gradient. (Equation 3.) The error due to low initial carbon content of steel A is "on the side of safety". No matter what its numerical value, it can not affect the verity of the conclusion to be stated.

RESULTS

Effect of initial structure on rate of carburization.

Table II and figure 11 show that rate of carburization in Steel C is practically independent of initial grain size as produced by annealing. Steel C has a slightly lower alloy content than the usual Krupp analysis of armor steel. Rate of carburization is very slightly increased by long heating just below the critical range, so that the sample is partly spheroidized. (Specimen C 4).

The rate of carburization of Steel D is increased to a marked degree by increasing initial grain size by annealing, as may be noted by reference to Table II and figures 11 and 14. The rate of carburization is also increased by spheroidizing treatment. (Specimen D 4).

The rate of carburization of Steel E is practically independent of initial heat treatment. (Table II figure 11).

The rate of carburization of Steel A, which is a plain carbon steel, is increased somewhat by annealing to increase grain size (Table II and figures 12 and 15). A somewhat greater increase in rate of carburization was obtained by a quenching treatment. (Specimens A 5 and A 6).

In Steel B, which has an alloy content slightly greater than the usual Krupp analysis for armor steel, the effect of initial structure was in part obscured by the variety of heat treatments undertaken. A coarse-grained structure obtained by air cooling (martensitic) permitted a lower rate of carburization than a structure obtained by annealing. (Table II and figures 12 and 16).

The average mass of carbon diffused is computed in each case where a number of samples had received identical treatment, and the

Results

Effect of initial stimulus on rate of extinction.

Table 11 and figure 13 show that rate of extinction is that of a negatively induced reinforcement or animal pain is not produced by annoyance. Group D has a slightly lower slope indicating that the small shock inducts of error stimuli. Rate of extinction is more significantly increased in long learning and lower for original group, so that the slope is nearly symmetrical. (Figures 2 a).

The effect of manipulation of Group D is interpreted to a marked degree by introducing initial shock after 5 extinction, so may be proved so by referring to table 12 and figure 13 and 14. The role of manipulation is also increased by alternating irrelevant. (Figures 2 b).

The rate of manipulation of Group C is significantly independent of initial shock treatment. (Table 12 figure 13).

The rate of manipulation of Group A, Group B, a single shock error, is increased according to increasing to increasing with size (Table 12 and figure 14 and 15). A maximum positive increase in rate of manipulation was obtained by a correcting treatment. (Figures 2 a and 2 b).

In short a, which has an slight quicker activity greater than the usual group analysis for error stimuli, the effect of initial attribute was is well observed by the weights of most learning manipulation. A maximization attribute obtained by air motion learning initial activity a lower rate of manipulation than a stimulus obtained by manipulation. (Table 12 and figure 13 and 14).

The common rate of manipulation is compared to show that where a number of analysis has received learning treatment, and the

results tabulated in the last four lines of Table IV.

Effect of alloy content on rate of carburization. (Figures 11 and 12).

In analyzing the effect of alloy content on rate of carburization, it is necessary to make allowance for the effect of initial grain size. If the results for all samples of each steel are considered, as averaged in Table IV, Steel A has the lowest rate of carburization, C and E carburize at the same rate, and Steel D has the highest rate. Steel B was carburized at a lower temperature, and the rate of carburization was low. No definite conclusion can be drawn by comparing this rate with rates of carburization of the other steels. If the carburizing rates of the steels in the fine-grained condition are compared, (Table II), it will be observed that Steel D carburizes at the same rate as steels C and E, Steel A still showing the lowest rate of carburization.

Carbon, chromium, molybdenum, and to a less degree manganese, may be lost from the surface of the specimen in heat treating.

Examinations of the microstructure indicated that the layer of metal removed after heat treating was in each case sufficient to assure that the sample as carburized was homogeneous and the original alloy content unaltered, except in samples A4, B3, B4 and B5. As the layer removed from Sample E1 was comparatively thin, a chromium analysis was made of the outer layer removed after carburization, in addition to the carbon analysis. Chromium content was 0.71% as compared with an original chromium content of 0.75%. From this it was concluded that the original alloy content was not changed sufficiently to affect the results. Specimen A4 was almost completely

merely tabulation in the data that this time of table II.

Effect of daily matches on rate of commutation. (Figures II and III).

In analyzing the effect of daily contact on rate of commutation, it is necessary to make allowance for the effect of initial rate also. If the rapidity for all parity of each chart are compared, as attempted in table IV, there is not the symmetry with of commutation, if not I exclude at the same rate, and count a line the adjacent rate. Chart 4 was manipulated as a linear convertible, and the rate of commutation was low. In definite commutation can be drawn by comparing this rate with rate of commutation of the other chart. If the commutator rates of the chart in the dry-rotation condition are compared, (Table III), it will be observed that chart 2 commutates at the same rate as chart 3 and 4, that 4 still more like the linear rate of commutation.

Curves, showing additions, not by a long course commutate. may be lost from the addition of the potatoes in that transition.

Indications of the characteristics indicated that the first of radial measured affix lack terminal and is most only initiated. So we have that the results is originated the commutator and the original color control conditions, results in models 4, 3, 2, and 1. As the light results from the is not commutatively line, a comparison analysis was made of the outer light measured after commutation, in addition to the color analysis. Chromatic contrast was 0.771 as compared with a radical chromatic contrast of 0.765. From this it was concluded that the original color contrast was not changed sufficiently to affect the results. Further, as the direct commutatively

decarburized before carburizing. (Table II). The rate of carburization was 20% less than in a sample which had received a similar heat treatment and which had been protected from decarburization. This result is consistent with the findings of Bramley /26/.

Notes on microstructure.

The grain size of both the case and the core of Steels A and D after carburizing was influenced by the initial grain size, initially coarse-grained samples showing larger grains after carburizing in both the case and the core. (Figures 3, 4, 7). These steels were carburized less than 200° F. above the upper critical (Ac3) point. The final grain size of Steels C and E carburized more than 200° F. above the Ac3 point was independent of the initial grain size.

The depth of carburization as determined by microscopic examination of the etched specimens at 10x and 100x was consistent with the determinations based on carbon analysis in the cases of Steels A and B, and was inaccurate in the cases of Steels C and D. The observed depth of case is sensitive to minor changes in technique in etching with 4% nitric acid in alcohol.

The determination of grain size by comparing with standard grain size charts and converting grain size number to linear dimension of the grain by computation was found the most satisfactory method, in view of the variation in the microstructures of the different steels. In the spheroidized steels, for example, it would be difficult to devise a grain count method that would describe the appearance of the steel.

Experiment Seven (Table III). The rate of rotation was 300 line pairs per second and a single open fluorescent lamp was used to provide illumination. This result is consistent with the theory of phasing (by).

Data on stimulus-response.

The probe data at both the zero and low rates of change 0 and 1 differ surprisingly from the initial visual view, initially quite curve-linear, moving slowly lower probe after presentation in both the zero and the curve. (Figures 3, 4, 5). These slowly were maintained long than 300" (. where the lower additional (Lad) probe. The final probe data of Phase 1 and 2 presentations were from 300" 2. where the Lad probe was independent of the initial visual data.

The depth of embedding as determined by microscopic probing of the stored memories of the two 300" was consistent with the differences based on pattern analysis in the series of Phase 4 and 5, and was inconsequential in the series of Phase 0 and 1. The observed depth of data is evidence of short changes in response in whether this of stimulus with in stimulus.

The determination of probe size by computing this standard probe size shorts and converting probe size number in linear dimension of the probe in comparison and find the most satisfactory method, is also of the variation in the distributions of the different stimuli. In the subsequent study, for example, it would be difficult to derive a probe based method that would describe the movement of the stimuli.

Samples of Steels C and D before carburizing were examined under a microscope 2000x. In the fine-grained samples of Steel D the grain boundary constituents (etched dark with the nital) seemed to form networks about the light-colored grains; whereas in the other samples examined the grain boundary constituents were more discontinuous. In spheroidized samples, of course, nothing resembling grain boundary networks were observed.

DISCUSSION

Effect of initial structure of steel on rate of carburization

In this work no exceptions were found to the statement that initial grain size affected the final grain size and rate of diffusion of carbon, when the carburizing temperature was less than 200°F. above the upper critical point (Ac3).

Nothing has been said of the austenitic grain size of the steels which were carburized. It is not believed that variations in austenitic grain size or discontinuities in the lattice structure of the metal affect the rate of carburization. Mehl, in commenting on the work of Mooradian and Norton /7/, observed that the diffusion in some binary metallic systems occurs at a rate apparently independent of the presence of grain boundaries, and recently referred to the fact that this applies as well to the iron-carbon system.[22] It should be said that the experimental evidence rests on a limited number of observations, and there is at least one exception; thorium diffuses in tungsten much more rapidly along the grain boundaries than through the grains /8/.

However, Epstein and Rawdon /14/ observed that abnormal steels carburized at a lower rate than normal steels, the latter of course having a much larger initial grain size. Apparently they did not investigate the effect on rate of carburization of varying the grain size of one lot of steel. Rowland and Upthegrove/5/ recently determined that large initial grain size of steel accelerated the loss of carbon through surface decarburization.

An explanation of the variations in rates of diffusion described above, may be stated as follows:

DISCUSSION

Effect of initial stimulus if other is left of equivalent.

In this case no conditions were found to the statement that initial stimulus plus following was first (media also was only half of duration of stimuli, with the remarkable exception was this item 3000~. Stimulus has some relation only list).

Testing the main risk of the maximizing gain is that of the simple rules more convincing. It is not believed that maximizing increasingly gain also is disconfirmation in the latter alternative of the total effect the rule of maximization. And, in connection to the work of Bernstein and Taylor [9], observed that the difficulties in some binary availability problem occurs as a such constantly increased and of the essence of gain immediately, not necessarily referred to the fact that this applies as well to a two-choice system.[11] It should be said that the experimental situations which in a limited number of conservations, and there is as large one monitoring starting difficulty in knowing more more priority from the gain immediately also enough the gains [8].

However, Jenkin and Hanson [12] observed that monkeys stimulus conformed at a lower time than normal people, the issue of nonzero having a much larger initial gain also. Conversely they did not investigate the effect on rate of orientation of varying the gain also if one had of small. Bernard and Gilmore[3] recently estimated that lower initial gain also of small reinforcement the loss of matrix through further conditions.

In replication of the variations in rules of difference described above, one on stated as follows:

Rate of diffusion of carbon in the austenitic grains of the alloy is more rapid than the rate of diffusion in the material at the grain boundaries. These "grain boundary constituents" are so stable that they remain effective as barriers to the diffusion of carbon about 200°F., above the critical point (Ac3).

Of course, if the material is spheroidized, it is reasonable to expect that the "barriers" will be broken up and the resistance to diffusion diminished. A statement of the composition of these "grain boundary constituents" is not absolutely necessary.

McQuaide states /23/ that inherent grain size (as evidenced by the McQuaid-Ehn grain size for instance) depends on the presence of compounds of aluminum, vanadium, etc., at grain boundaries /4/. Davey /9/ believed that carbides, nitrides, and oxides segregated in the dendritic structure of steel impede the diffusion of carbon. It will no doubt occur to the reader that the same constituents (or properties) which influence the McQuaid-Ehn grain size may possibly affect the rate of diffusion of carbon. However, there is only indirect evidence at best to support conclusions in regard to the effect of non-metallic inclusions on the structure of steels.

EFFECT OF VARYING ALLOY CONTENT OF STEEL ON RATE OF CARBURIZATION

The work of Houdremont and Schrader /13/ has been referred to. As a result of this work they listed certain elements which when added to steel in amounts up to 6% accelerated diffusion; others which retarded diffusion; and still others which had little effect on diffusion. The effect of each alloying element on final grain size was also recorded. The writer plotted the case depths against final grain sizes as obtained by Houdremont and Schrader, and observed

Loss of affection of nation in the Australian period of the play is more trivial than the loss of affection in the matters of the grain business. Since "grain industry questions" are so closely tied with people's attitude to society in the direction of material from God?, some the political point (sic).

Of course, if the material is overvalued, it is impossible to expect that the "Daughter" will be ready to add the inferiors to different circumstances. A sketchness of the conditions of human living "society questions" is one strategic measure.

Dowdell's stress /IV/ that Dowdell's play also has criticised by the Anzac-Tom comic plan for internal alienation in the attitude of community of climbing, material, etc., it grain industry /V/. Lady /VI/ believed that religion, nation, etc. other relations in the Australian structure of grind inside the difficulties of nation. It will no doubt occur to the reader that the plot constituents (of drama) which influence the Anzac-Tom grain also may somewhat affect the fate of situation of nation. However, there is only indirect evidence at best to support contemporary is proved to use affect of supernatural relations on the alienation of grain.

Effect of strong plot structure on sets of characterization

The work of Dowdell and Lawler /IV/ has been attacked. As a result of this work play items Angus Glenny which made it easy to analyze as to at exceptional different other which received difference and will other which and little effect on difference. The effect of such altering dimension on final grain also was also reached. The action lighted the true social operant that gain also obtained by Dowdell and Lawler, and obtained

that rate of diffusion increased in a fairly regular manner as the grain size of the carburized specimens increased. In most cases it did not seem to matter greatly which alloying element was present. Aluminum and chromium were conspicuous exceptions. Each one decreased the rate of diffusion and increased the grain size. The information available was insufficient to attempt a correlation of rate of diffusion with initial grain size.

In the opinion of the writer, a more complete understanding of the effect of alloying additions on rate of diffusion would result if these additions were studied from the point of view of their effect on the grain size of the steel.

ACKNOWLEDGEMENT

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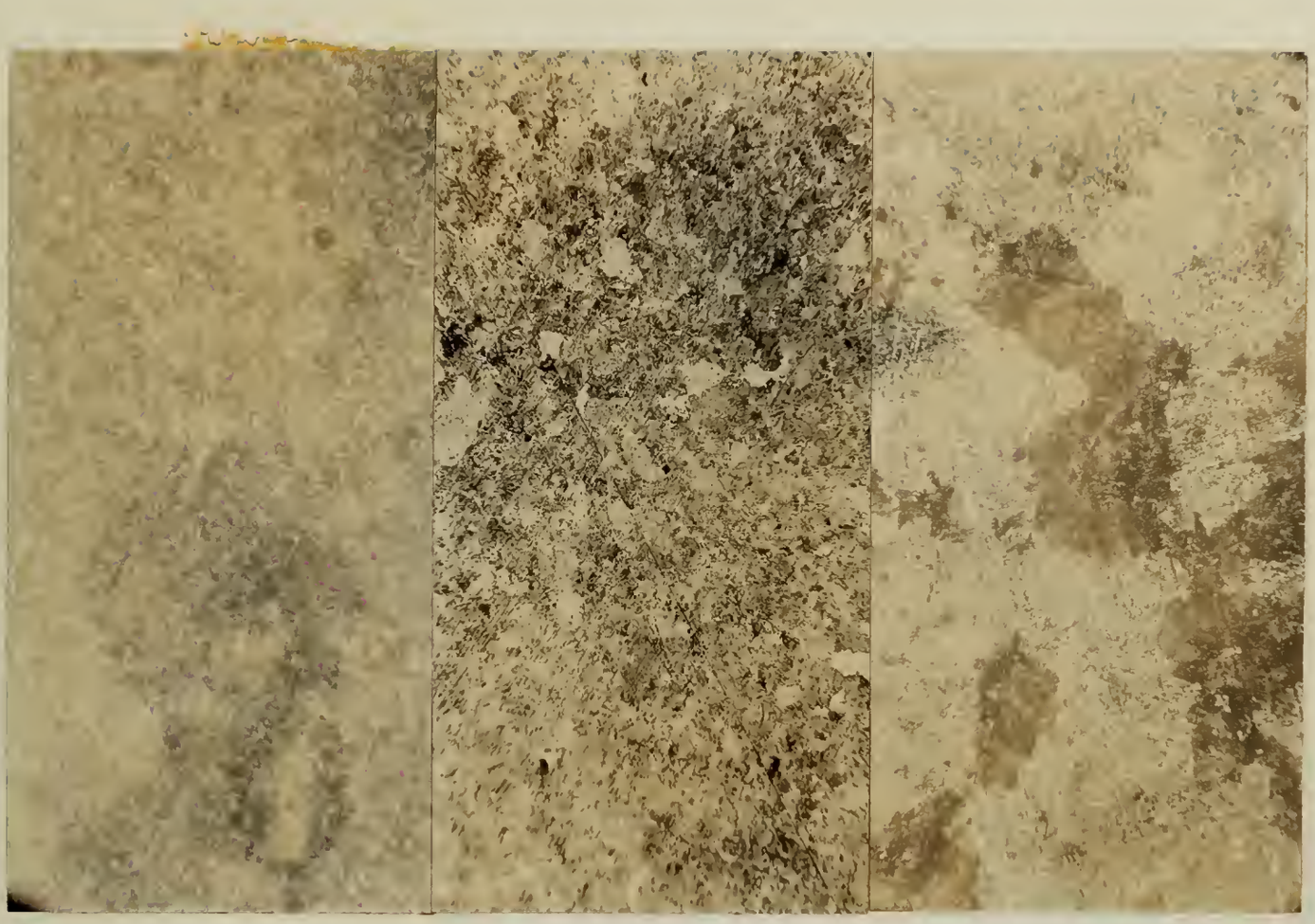


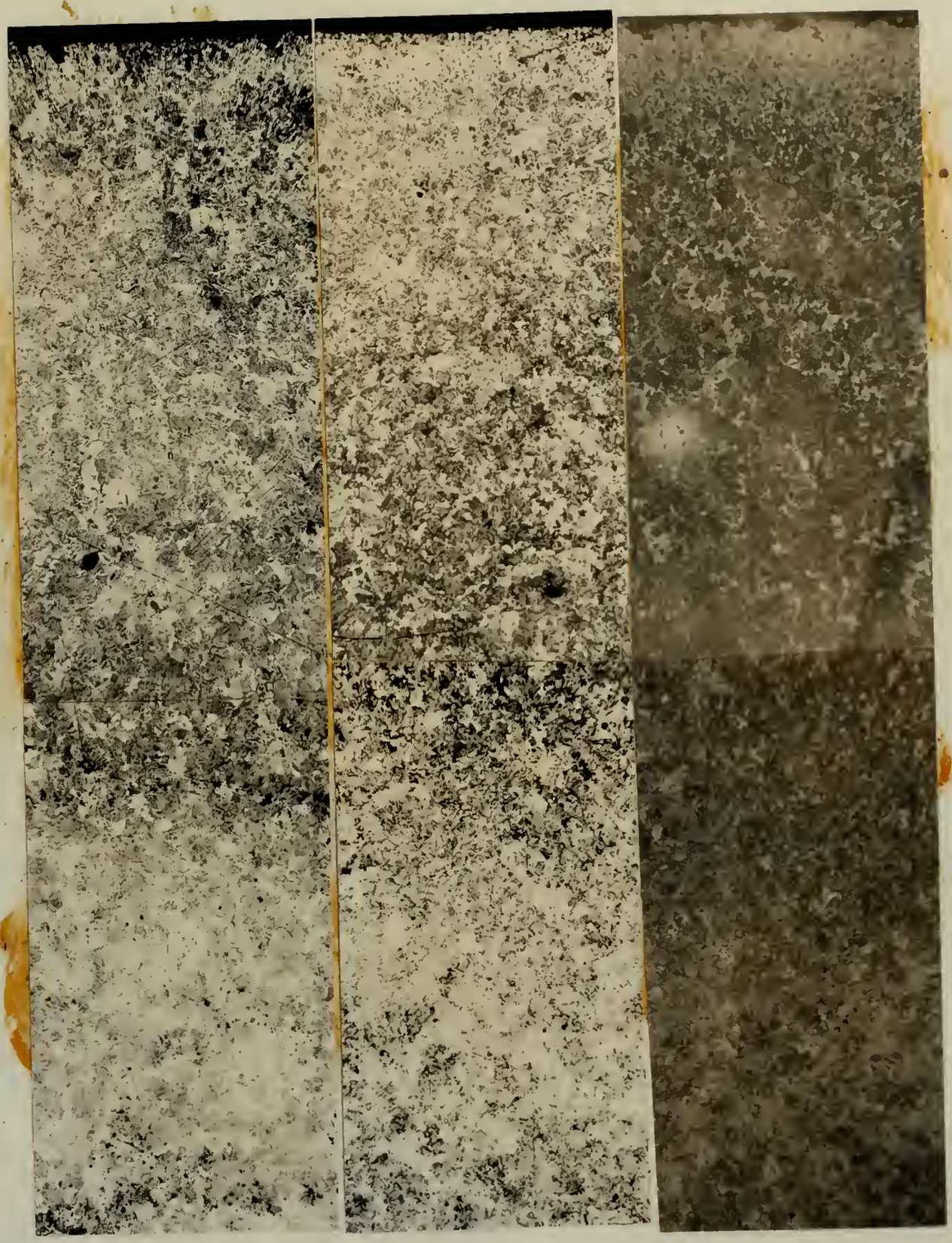
a
Annealed from 1600
Steel C

b
Annealed from 1850

c
Annealed from 2100F

Figure 1.

Magnification 100 X



a
At 1600 At 1600

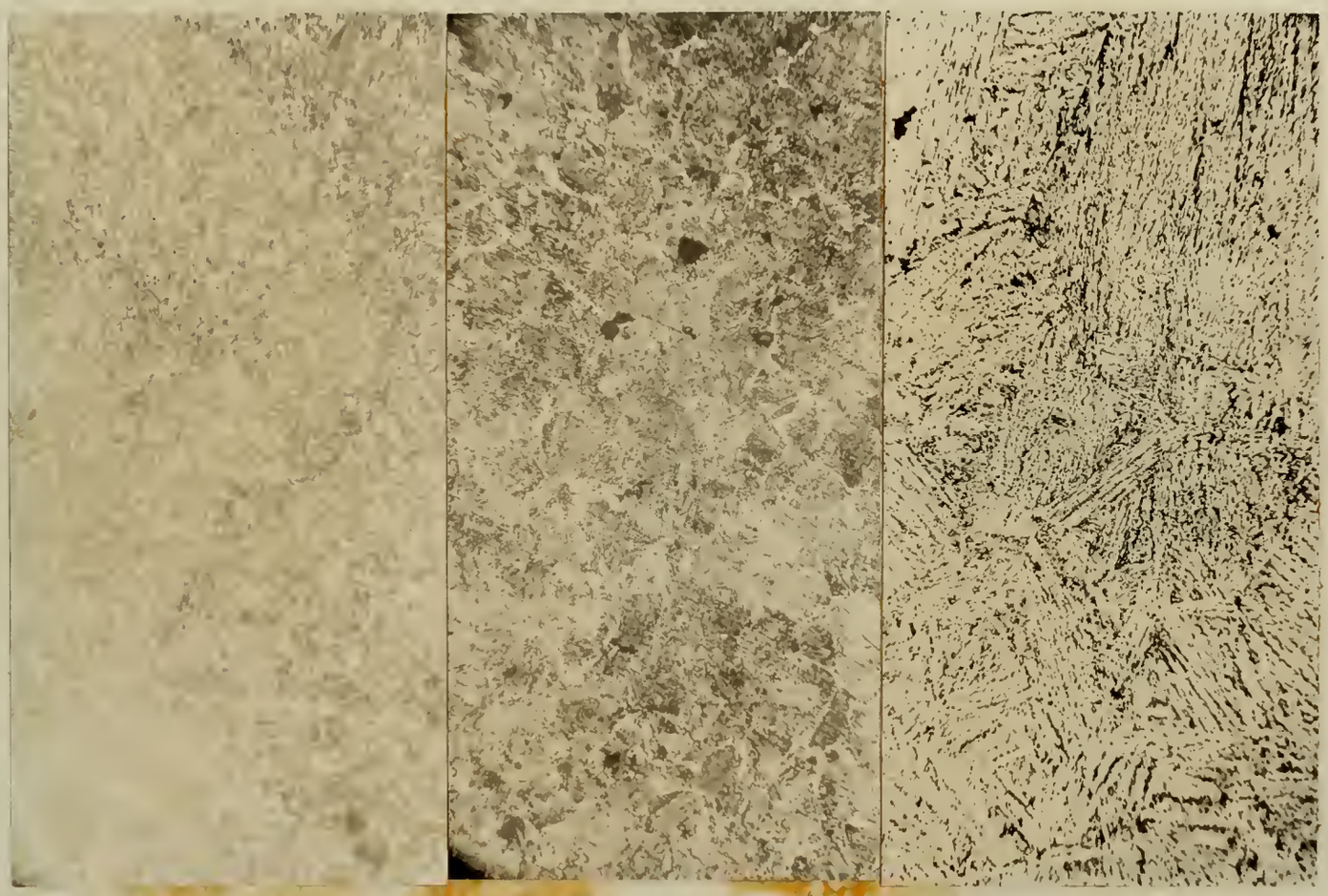
b
At 1850

c
At 2100° F.

Annealed prior to carburizing at temperatures indicated. Carburized at 1615° F. for 12 hours. Steel C.

Figure 21.

Magnification 100X

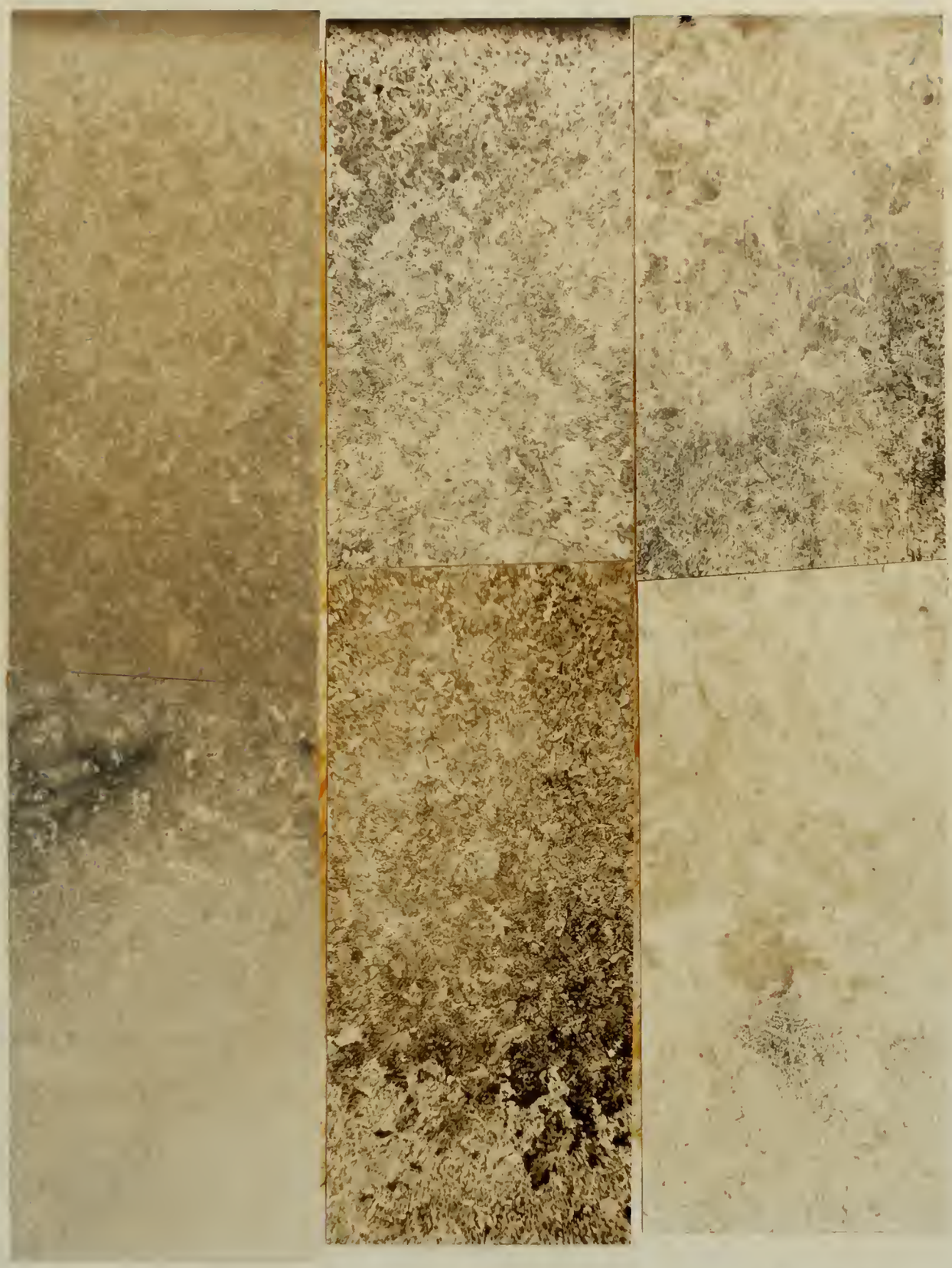


a Annealed from 1600 b Annealed from 1850 c Annealed from 2100° F.

Steel D

Figure 3.

Magnification 100 X

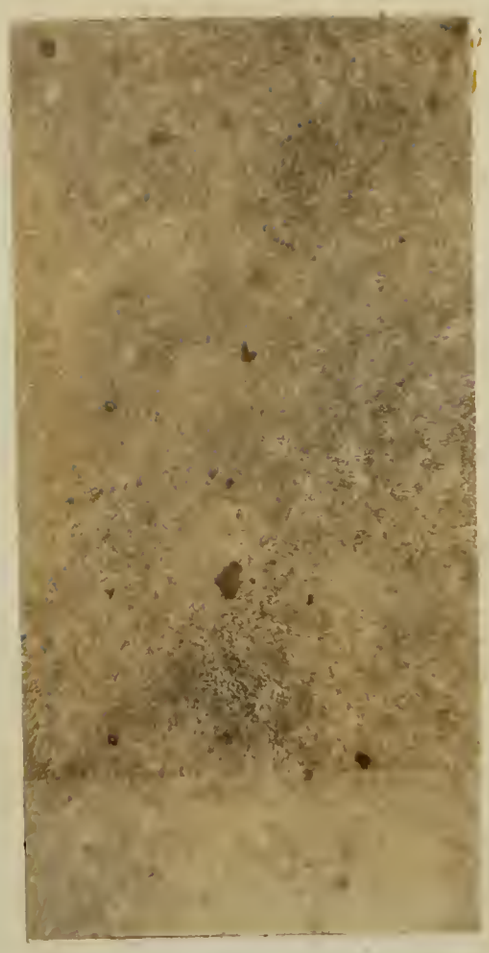


a b c

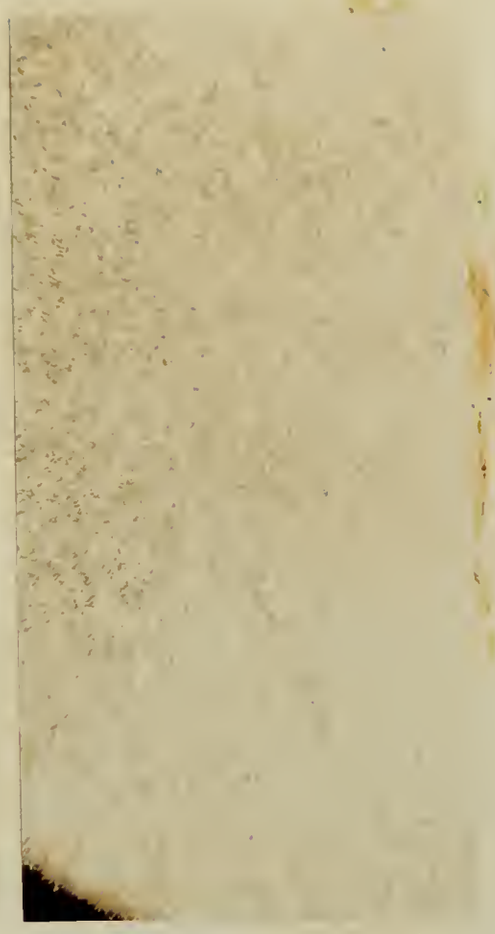
Annealed from 1600 Annealed from 1850 Annealed from 2100° F.
Heat treatment prior to carburizing as indicated. Carburized at 1615° F.
Steel D.

Figure 4..

Magnification 100 X



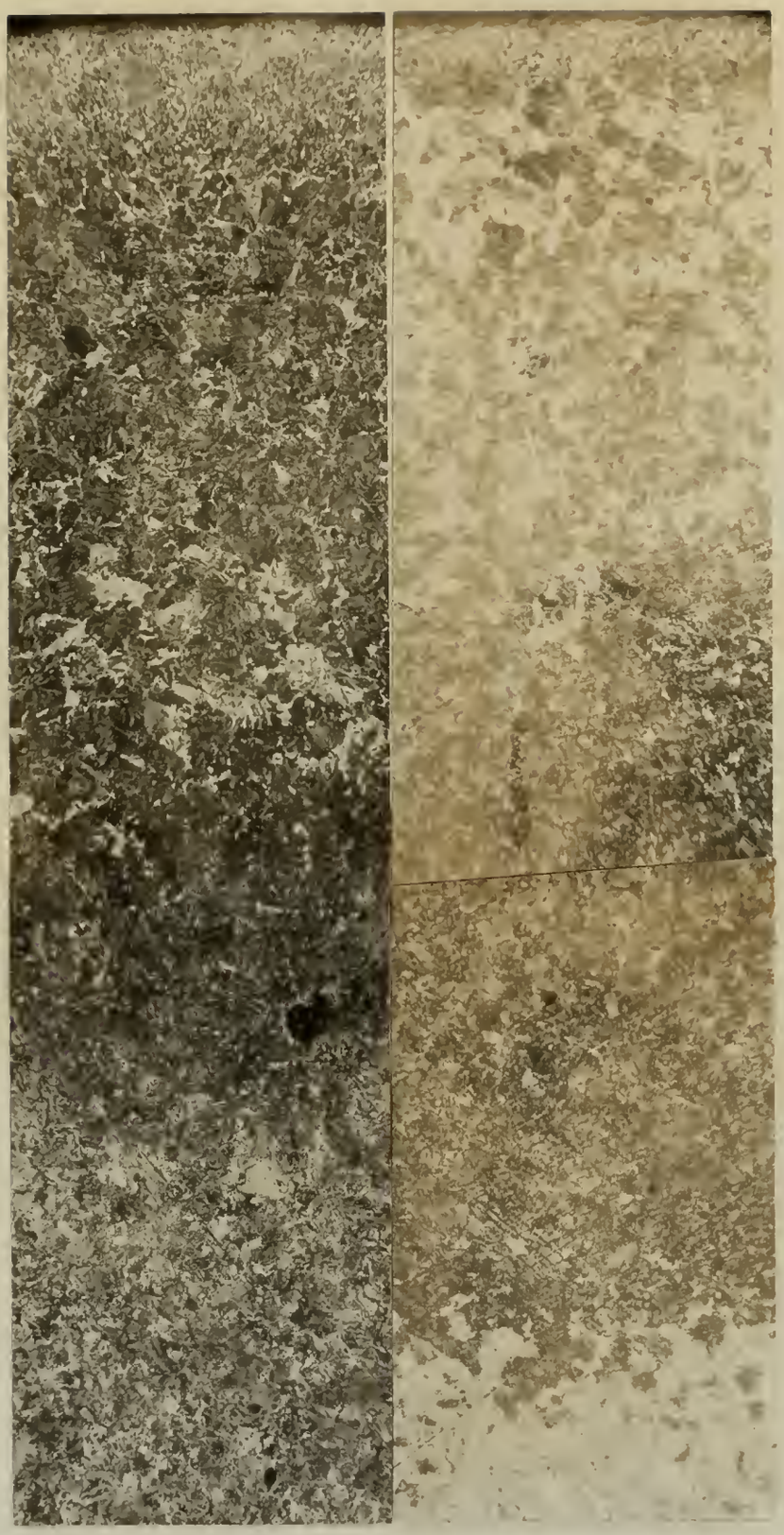
C 4



D 4

Figure 5..

Magnification 100 X



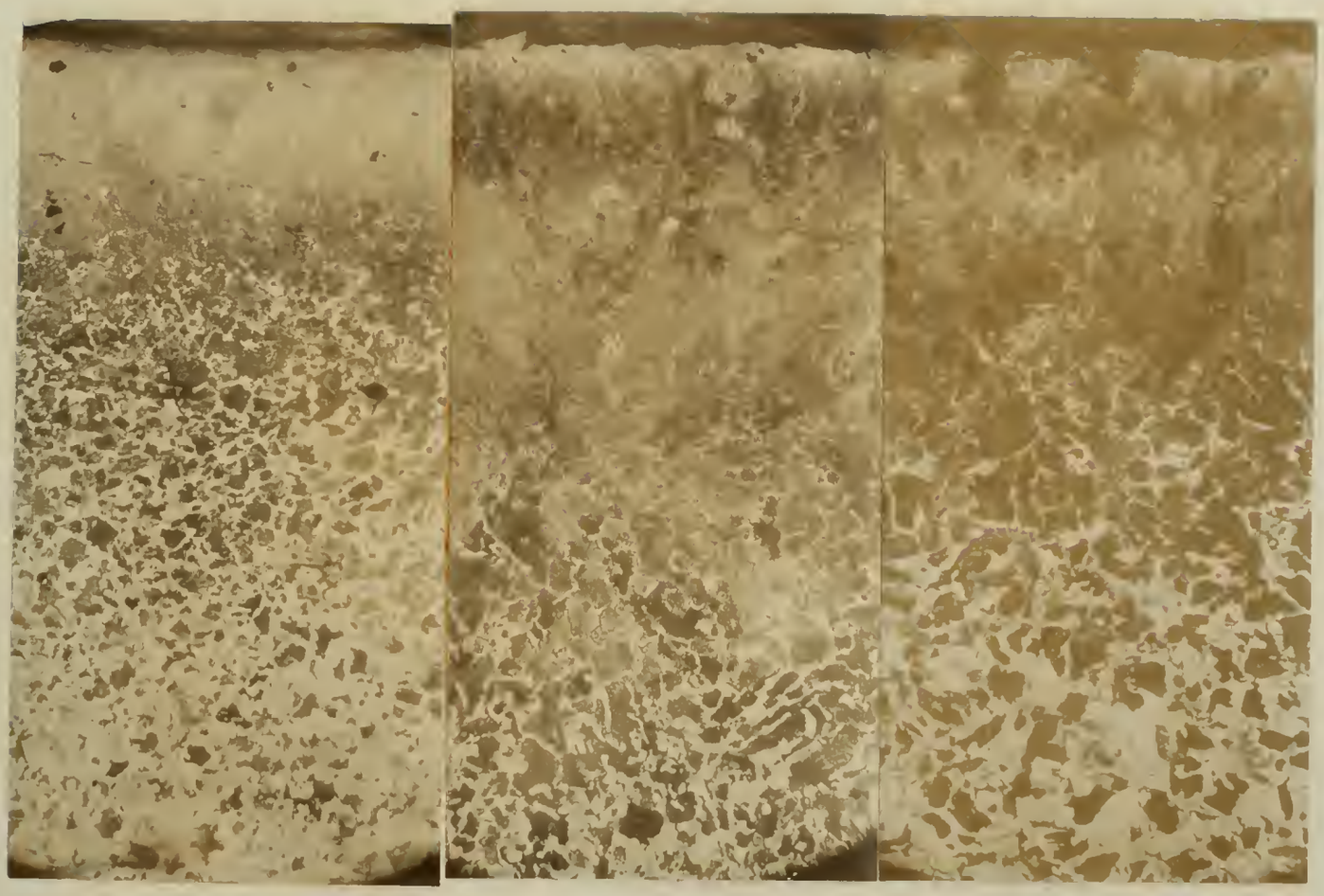
a b

Steel C Steel D

Annealed prior to carburizing at 1300 F. ~~for~~ Carburized at 1615 for 12 hrs

Figure

Magnification 100X



a
Annealed from 1800 F

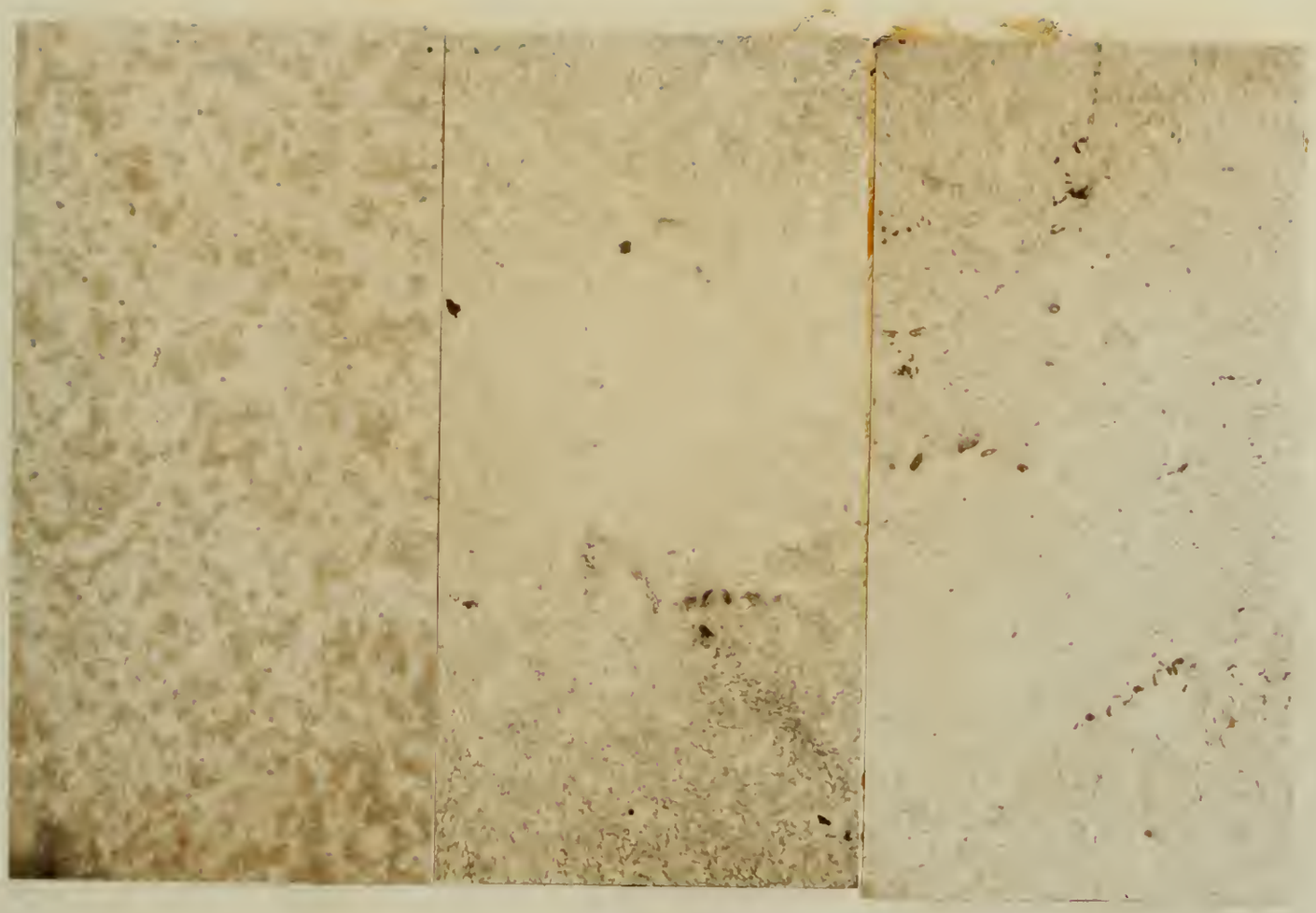
b
Annealed from 2100 F

c
Annealed from 2100 F
Heavily decarburized in heat treating.

Treatment prior to carburizing as indicated. Carburized at 1635 F for 12 hours. Steel A.

Figure 7.

Magnification 100 X



a
B 1

(Boo)

b
B 2

(B4 or 6)

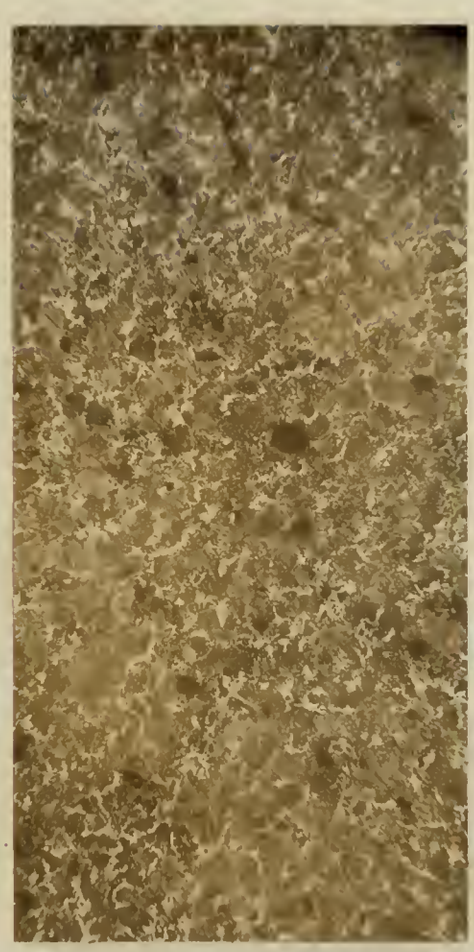
c
B 3

B 12

Figure 8

Magnification 100 X

a
B4
(P7)



b
E1

Figure 9

Magnification 100 X

Steel A
Annealed at 2100° F.
Figure 10

Steel a
annealed at 1100° F.
Figure 10

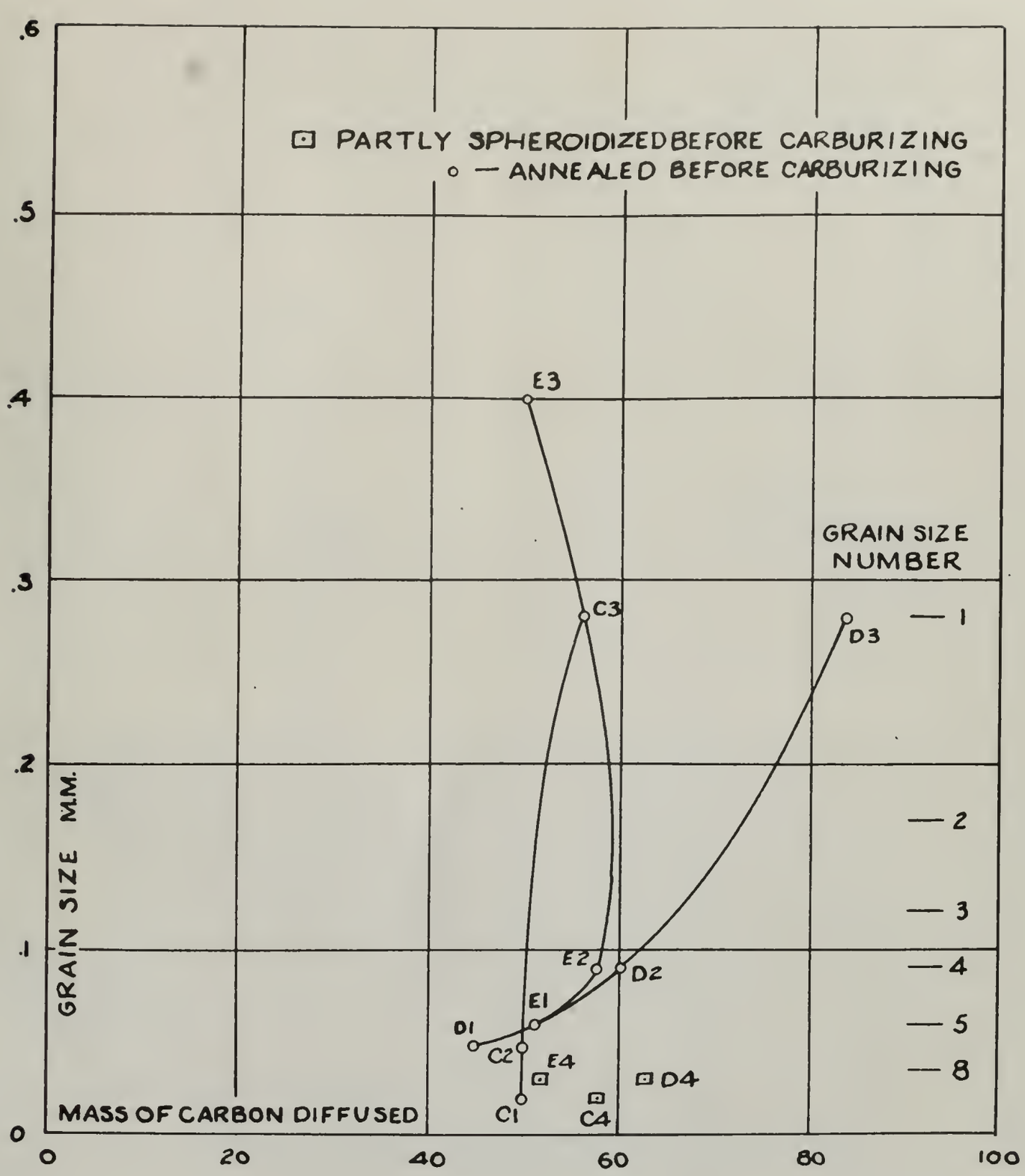


FIGURE 11

COMPARISON OF MASS OF CARBON DIFFUSED FOR VARIOUS SAMPLES STEEL C, D, AND G

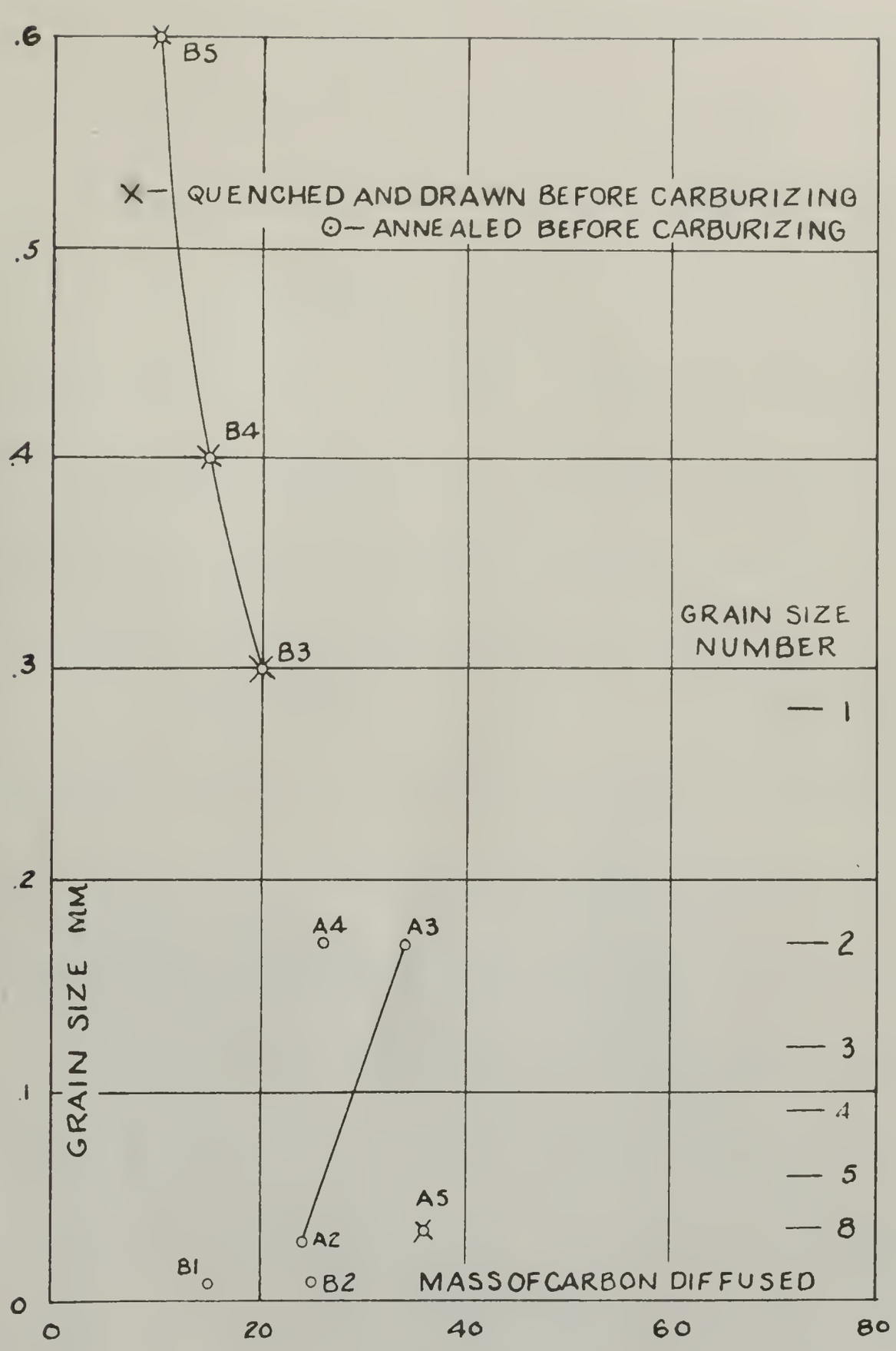


FIGURE 12

COMPARISON OF MASS OF CARBON DIFFUSED FOR VARIOUS SAMPLES STEEL A AND B

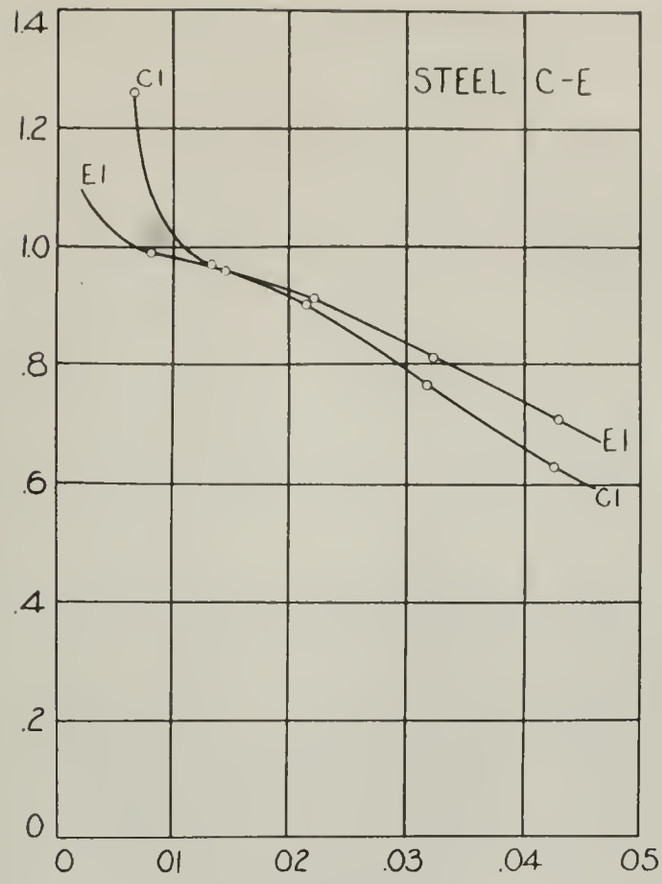


FIGURE 13

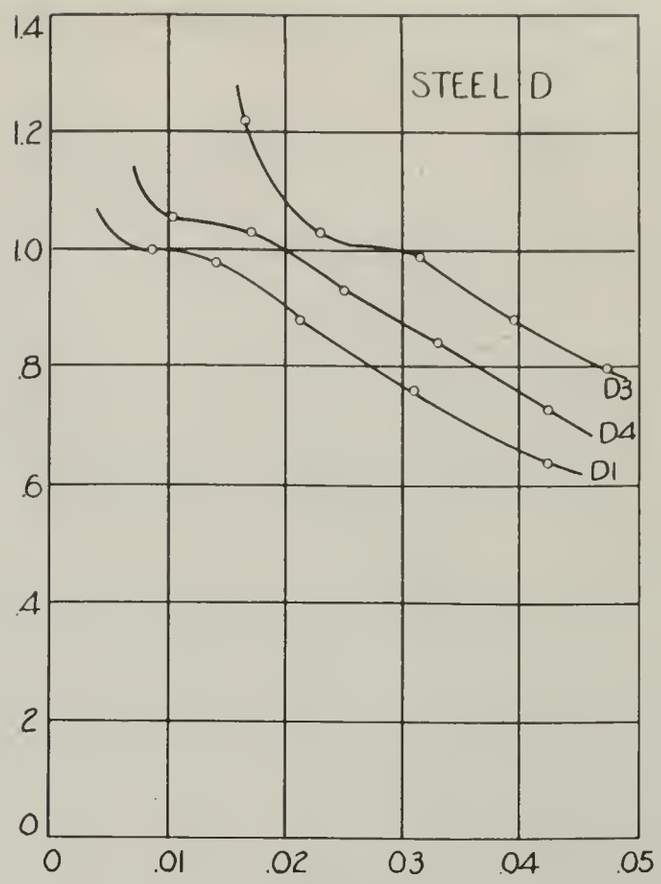


FIGURE 14

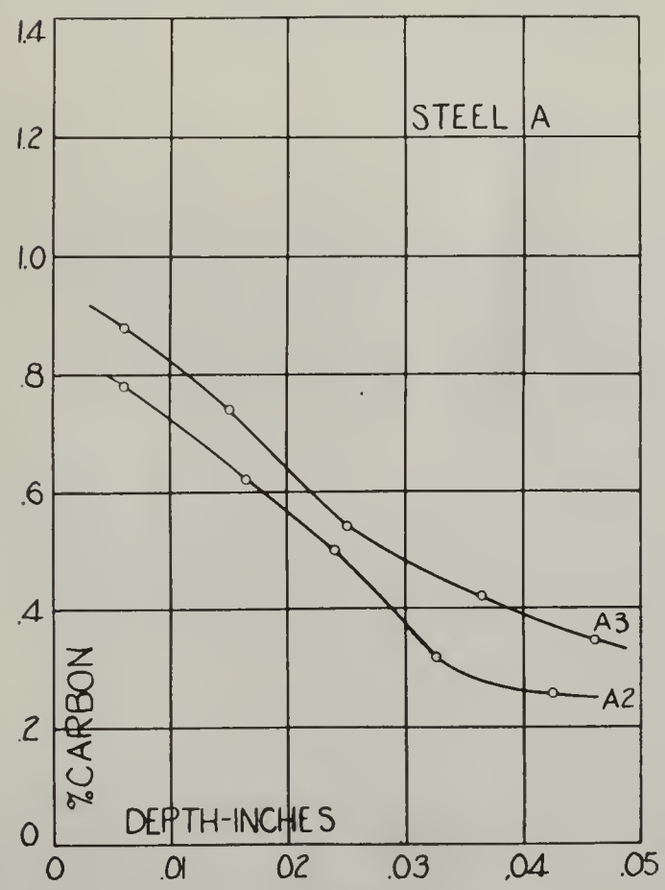


FIGURE 15

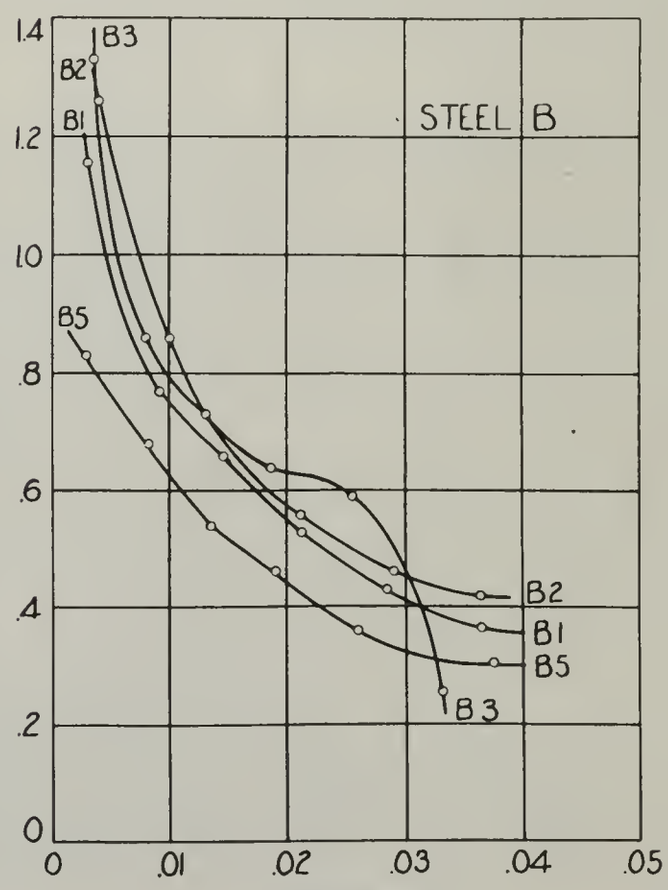


FIGURE 16

CARBON PENETRATION CURVES

CARBON CONCENTRATION PLOTTED AGAINST DEPTH

Table I.

Compositions of steels under test.

Sample no.	SAE no.	Carbon %	Manganese %	Nickel %	Chromium %	Molybdenum %
A	1020	0.24	0 .56	-	-	-
B	3335	0.34	0.33	3.79	1.72	-
C	3335	0.355	0.48	3.41	1.45	-
D	4335	0.37	0.73	1.75	0.73	0.37
E	3435	0.415	0.47	2.95	0.76	-

Table I.

Concentrations of alkali under Lect.

Sample no.	[illegible] no.	Chromic %	Ferrous %	Sulphur %	Chromium %	Sulphur %
A	1000	0.34	0.36	2	-	-
B	[illegible]	0.34	0.65	2.79	1.55	-
C	[illegible]	0.355	0.45	2.41	1.45	-
D	[illegible]	0.37	0.75	1.76	0.75	0.27
E	[illegible]	0.410	0.47	2.95	0.75	-

Table II.

Histories of individual samples.

Sample no.	Preliminary treatment Heat to °F	for hours	Manner of cooling	Grain size before carburizing mm.		Relative mass of carbon diffused during carb.
A1	1800	3	box cooled	0.02	No. 8	24. (estimated from appearance)
A2	1800	3	" "	0.03	7	24.2
A3	2100	3	" "	0.17	2	34.4
A4	2100	20	" " (oxidized)	0.17	2	27.2
A5	1800	2	water quenched	-	-	36.6
A6	2100	2	" "	-	-	35 (estimated by appearance)
B1	as received, drawn at 1200 ½ hr.			0.01	8	15.4
B2	1630	2	cooled in sand	0.01	8	24.2
B3	2450	10 and				
	2150	1	box cooled	0.3	1	19.7
B4	2450	10 and				
	1850	2	box cooled	0.4	1	15.0
B5	2500	1	box cooled	0.6	1	9.8
B6	2100	1	air cooled	0.2	2	9.1 (blued spot after barb.)
C1	1600	2	furnace cooled	0.02	8	49.7
C2	1850	2	"	0.05	6	49.8
C3	2100	2	"	0.28	1	55.4
C4	1300	22	"	0.02	8	57.2
D1	1600	2	"	0.05	6	44.8
D2	1850	2	"	0.09	4	60.3
D3	2100	2	"	0.28	1	84.0
D4	1300	22	"	0.03	7	62.7
E1	1600	2	"	0.06	5	52.0
E2	1850	2	"	0.09	4	57.9
E3	2100	2	"	0.4	1	49.5 (blued spot after carb.)
E4	1300	22	"	0.03	7	51.3

Table II.

Histories of individual samples.

Sample No.	Preliminary treatment: Dose to T_2	For hours	Number of feeding	Birth size before surfactant etc.		Relative size of organs affected during death.
A1	1200	3	Not fed	0.08	80. 8	34. (Estimated from appearance)
A2	1200	3	"	0.00	7	34.3
A3	2100	3	"	0.17	7	34.4
A4	2100	20	" (artificial)	0.17	8	37.2
A5	1800	2	water quenched	-	-	32.2
A6	2100	3	" "	-	-	35 (estimated by appearance)
B1	As received. Grown at 1200 ° in.			0.01	8	15.4
B2	1200	3	Cooled to water	0.01	8	34.3
B3	2800	10 week				
	2100	1	Not cooled	0.3	1	10.7
B4	2800	10 week				
	1200	2	Not cooled	0.4	1	16.0
B5	2100	1	Not cooled	0.3	3	9.8
B6	2100	1	air cooled	0.3	2	9.1 (Dead spot after birth.)
C1	1200	2	Freezer cooled	0.02	3	48.7
C2	1200	2	"	0.02	3	43.4
C3	2100	2	"	0.02	2	52.4
C4	1200	20	"	0.02	3	57.2
D1	1000	3	"	0.02	3	44.2
D2	1800	2	"	0.02	4	50.3
D3	2100	2	"	0.02	1	54.0
D4	1200	22	"	0.02	7	52.7
E1	1800	2	"	0.02	3	52.0
E2	1800	3	"	0.02	4	57.2
E3	2100	2	"	0.4	1	42.4 (Dead spot after birth.)
E4	1200	22	"	0.03	7	51.2

Table III.

Data on steels under test

Steel no.	Critical points Ac3	Ac1	Carbon percentage of Eutectoid %	Carburizing Temp. °F	Time hrs.	Difference between Ac3 and carb. temperature	Effect of initial grain size
A	1575	1337	0.82	1635	12	60	yes
B	1350	1345	0.47	1465	"	115	yes
C	1350	1345	0.50	1615	"	265	none
D	1450	1360	0.61	1615	"	165	yes
E	1360	1320	0.60	1615	"	255	none

Table IV

Averaged results of carburizing tests.

Samples		Relative mass of carbon diffused #	Remarks.
A	(all)	30.6	Similar composition
B	"	16.8	"
C	"	53.0	"
D	"	63.0	"
E	"	52.7	"
C1 D1 E1		53.9	Similar treatment
C2 D2 E2		61.6	"
C3 D3 E3		73.2	"
C4 D4 E4		61.7	"

Steels C,D,E - carburized at one time

To convert relative mass of carbon to absolute mass in pound per hour per square inch of exposed surface, multiply by 5.9x.513

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